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# The Color Change of Natural Green Sapphires by Heat Treatment

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**Abstract**

This research aimed to investigate the effects of heat treatment on color and clarity of green sapphires. The Green sapphires were heated at sequentially increasing temperature of 1300, 1400, 1500 and 1600 °C in oxygen atmosphere. At each treatment temperatures, the samples were treated for 40 hours with their color and clarity were measured before and after heat treatment at each temperature. It was found that, when green sapphires were heated at high temperatures, the color of the untreated sapphire crystal changed to yellow at higher temperatures. Whereas, there were no significant changes in the clarity of all samples found in the temperature range of 1300-1600 °C.



*Keywords:* Green sapphires, heat treatment

## 1. Introduction

The structure of Green sapphire is related to corundum ($Al_2O_3$) and involves the $Al^{3+}$ ions being distributed in an ordered fashion in 2/3 of the distorted (trigonal) octahedral sites within a frame work of hexagonal close-packed $O^{2-}$ ions. The color of ruby arises mainly from $Al^{3+}$ ions being replaced by 3d transition ions during a crystallization process. This is possible because the size of 3d transition ions is very close to that of $Al^{3+}$ (0.57 Å) [1].

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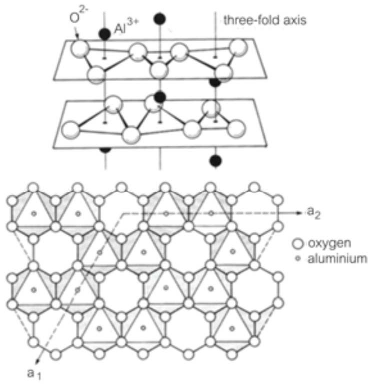



Fig. 1. A polyhedral model of the structure of corundum [1]

The presence of varying amounts of $Cr^{3+}$ ions gives color to ruby from pink (0.01 mole %) to deep red (2 mole %) [1]. Iron usually exists in both $Fe^{2+}$ as well as $Fe^{3+}$ depending on the number of $O^{2-}$ vacancies and other point defects [2]. $Fe^{3+}$ and $Ni^{3+}$ in corundum yield yellow color whereas $Fe^{2+}$ gives sapphire green color instead [3]. The charge transfer mechanism between $3d^6$ ($Fe^{2+}$) and $3d^0$ ($Ti^{4+}$) bands effectively gives sapphire its blue color. A combination of these $Fe^{2+}$, $Ti^{4+}$ and $Cr^{3+}$ ions is clearly responsible for bluish red in ruby [4]. More detailed coloring mechanisms and impurity ions present in sapphires are listed in Table 1.

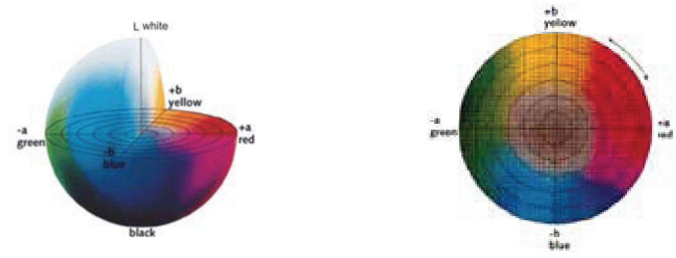
Table 1. 3d Transition ions coloring gem corundum ($Al_2O_3$) [5]

| Sapphire Color | Verneuil Synthetics | Natural Coloring Ions | Coloring Mechanisms |
|---|---|---|---|
| Colourless | Pure | None | None |
| Ruby | $Cr^{3+}$ | $Cr^{3+}$ | Electronic transitions & Fluorescence |
| Pink | $Cr^{3+}$ | $Cr^{3+}$ | Electronic transitions & Fluorescence(R-line) |
| Blue | $Fe^{2+}$,$Ti^{4+}$ | $Fe^{2+}$, $Ti^{4+}$ | Charge transfer |
| Purple and Violet | $Cr^{3+}$,$Fe^{2+}$,$Ti^{4+}$ | $Cr^{3+}$, $Fe^{2+}$, $Ti^{4+}$ | Electronic transitions , Charge transfer & Fluorescence(R-line) |
| Yellow | $Ni^{3+}$ | $Fe^{3+}$+ color centers | Electronic transitions |
| Orange | $Ni^{3+}$, $Fe^{3+}$ | $Fe^{3+}$, $Cr^{3+}$ +color centers | Electronic transitions & Fluorescence(R-line) |
| Green | Cobalt, Vanadium + Nickel | $Fe^{2+}$ | Electronic transitions |

The goal of this work was to investigate the effect of heat treatment on color of natural green sapphire measurements by spectrophotometer.

## 2. Materials and Methods

The natural green sapphires were cleaned thoroughly with acid and solvent to remove all stains and other impurities on their surfaces. Four crystal samples were chosen to determine trace elements by LA-ICP-MS. Then, the transmission spectrum of samples were measured by a spectrophotometer(Perkin Elmer Instruments model Lambda 800) before and after 40 hours of each temperature of sequential heat treatment in electric furnace at 1200, 1300, 1400, 1500 and 1600 $^{o}$C under oxygen atmosphere. Then, the transmission spectra were converted to CIE color index. The CIE color index used Lab color space in three dimensions is shown in Fig. 2(a) and in two dimensions is shown in Fig. 2(b).




(a) (b)

Fig. 2. CIEL*a*b* color index, (a) in three dimensions and (b) in two dimensions

## 3. Results and discussion

The results on the investigation of the trace elements in natural green sapphires before heat treatment are shown in Table 2.

Table 2. the trace elements concentration (ppm) of natural Vietnamese blue sapphires

| Sample | B | Mg | Ca | Ti | V | Cr | Fe | Ga |
|---|---|---|---|---|---|---|---|---|
| 1 | 44.98 | 10.08 | 92.56 | 113.47 | 9.31 | 4.30 | 6310.44 | 191.69 |
| 2 | 40.65 | 19.02 | 15.02 | 568.33 | 14.22 | 4.39 | 6789.78 | 212.94 |
| 3 | 33.85 | 20.53 | 22.24 | 176.45 | 9.16 | 36.93 | 1627.41 | 190.91 |
| 4 | 37.82 | 11.22 | 46.51 | 88.81 | 15.41 | 2.88 | 6198.53 | 165.97 |
| Average | 39.32 | 15.21 | 44.08 | 236.76 | 12.02 | 12.12 | 5231.54 | 190.37 |

From Table 2, it was found that the natural Vietnamese blue sapphires contain 98 %wt of $Al_2O_3$, B (39.32 ppm), Mg (15.21ppm), Ca (44.08 ppm), Ti (236.76 ppm), V (12.02 ppm), Cr (12.12 ppm), Fe (5231.54 ppm) and Ga (190.37 ppm) as trace elements.

The absorbance spectra of samples before and after the heat treatment are depicted in Fig. 3 and Fig. 4, respectively. In Fig. 3, the evolution shows the appearance of many absorption bands, the absorbance bands near 450, 388 and 377 nm are attributed to $Fe^{3+}$/ $Fe^{3+}$ pairs, $Fe^{3+}$ and $Fe^{3+}$/ $Fe^{3+}$ pairs, respectively. A small poorly resolved peak at about 860 nm was assigned to $Fe^{2+}$ and a broader peak around 560 nm is associated with $Fe^{2+}$-$Fe^{3+}$ charge transfer. On the contrary, the absorption band corresponded to iron in ferrous state ($Fe^{2+}$) is not present in the absorbance spectra of after treated samples at 1600 $^{o}$C, as shown in Fig. 4.

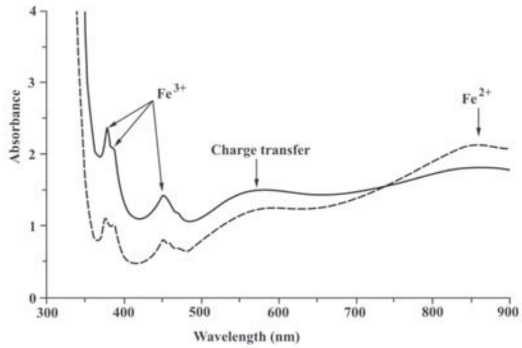



Fig. 3. Absorption spectra from 300 to 900 nm of untreated blue sapphire samples (2 pieces)

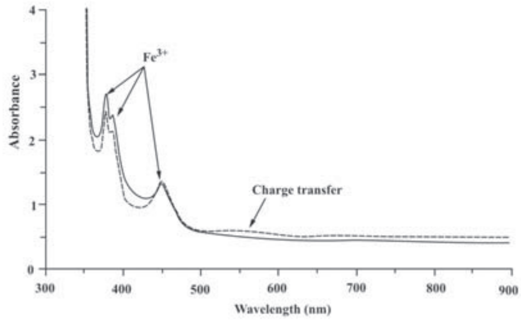



Fig. 4. Absorption spectra from 300 to 900 nm of Be-treated samples which became yellow sapphires (2 pieces)

The results of color measurements of three samples for the study of color change and clarity before and after heat treatment are shown in Table 3 and Figure 5.

Table 3. CIEL*a*b* color index of three samples before and after heat treatment at the temperatures range 1300 – 1600 °C

| Temperature (°C) | CIE L*a*b* color index | | |
|---|---|---|---|
| | L* | a* | b* |
| RT | | -4.55 | 9.44 |
| 1200 | 58.45 | -4.74 | 11.87 |
| 1300 | 52.21 | -4.02 | 12.34 |
| 1400 | 52.17 | -4.96 | 19.95 |
| 1500 | 53.13 | -4.35 | 13.53 |
| 1600 | 50.28 | -4.87 | 17.19 |

From Table 3 and Fig. 5, the green sapphires were heated at higher temperatures, the b* index of samples increases, or green color of the untreated sapphire crystal (RT) changed to yellow after heat treatment at high temperatures in oxygen atmosphere.

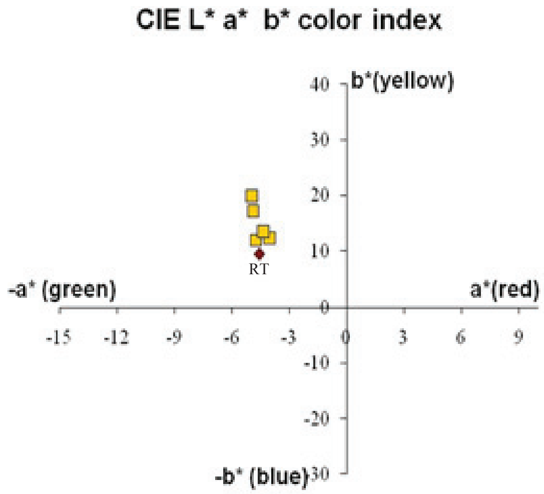



Fig. 5. CIEL*a*b* color index of green sapphires, before and after heat treatment in oxygen atmosphere

## 4. Conclusion

From results, it can be concluded and confirmed that the yellow coloration by heating under $O_2$ is of the same oxidation process which iron acts as the most important agency. By heating under oxidizing conditions, the oxidation processes of $Fe^{2+}$ by gaseous oxygen to be considered are

$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}$$

or, as the oxide:

$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

or in corundum

$$2Al_{2-2x}Fe_{2x}O_{3-x} + xO_2 \rightarrow 2Al_{2-2x}Fe_{2x}O_3$$

The above three equations are equivalent and result in an electrically neutral state containing only $Fe^{3+}$; in corundum, the result now corresponds to $Fe_2O_3$ being present in $Al_2O_3$, having a pale-to-medium yellow color, depending on the concentration. Heat treatment can reduce or eliminates the green color.

In conclusion, the cause of yellow coloration in heated green sapphires is actual reason is the charge transfer between the ferrous and ferric states of iron. The entails heating of the stone in an oxidizing atmosphere produces the following reaction:

$$Fe^{2+} \xrightarrow[\text{atmosphere}]{\text{heat in an oxidizing}} Fe^{3+}$$

with the conversion of the ferrous state to the ferric state, resulting in a yellow color replaces the green. $Fe^{3+}$ may be present as isolated ions scattered around the substance. Generally, as the concentration of these iron ions increases, the intensity of the yellow color increases proportionally [6]. Furthermore, the produced color is stable under the fading test.

## Acknowledgements

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